

CHARACTERIZATION AND MONITORING OF DENSE NON-AQUEOUS PHASE LIQUIDS

TECHNOLOGY DESCRIPTION

The main thrust of work this year has been to transfer the successes and lessons learned from the development and deployment of innovative dense non-aqueous phase liquids (DNAPLs) characterization technologies. This is being addressed in two ways. The first is the field application of selected technologies at two actual DNAPL sites in different parts of the United States. In addition to the fieldwork to augment the site's characterization strategy, a presentation will be made on DNAPL characterization and innovative DNAPL techniques. The second method for information transfer is the inclusion of a DNAPL module in the U.S. Environmental Protection Agency (EPA) Field-Based Site Characterization Technologies Course. Both methods of communication will emphasize the technological achievements of the previous work performed in this task and the strategy of using multiple complementary tools to tackle difficult characterization problems. The strategy and tools target the case of DNAPLs occurring in thin, highly discrete zones typical of most sites. The innovative DNAPL characterization tools that have proved to be most successful in field tests to date include:

- Hydrophobic sorbent ribbon on FLUTE™ (also known as SEAMIST™) membrane.
- Laser-induced fluorescence (LIF), Raman, and Optical Cone Penetrometer Test (CPT) probes.

These technologies have been successfully demonstrated and will complement tools currently used or proposed by industry, the EPA, and the U.S. Department of Defense (DoD). The innovative characterization technologies, e.g., CPT-based Raman and FLUTE™, build on the baseline DNAPL characterization techniques and generally strive for direct detection of DNAPLs with minimal invasion and minimal investigation-derived waste (IDW). In addition to these technologies, several other promising technologies have been tested (e.g., alcohol micro injection/extraction through CPT, differential partitioning gas tracer tests, and measurement of radon partitioning to DNAPLs). These require some additional development work. All of the DNAPL research and development projects at the Savannah River Site (SRS) are selected based on targets driven by site cleanup goals and local and regional regulatory requirements.

A coordinated package of innovative DNAPL characterization tools is being developed and deployed. Each technology is carefully designed to:

- Unambiguously identify DNAPLs in the subsurface.
- Minimize secondary waste.
- Eliminate undesirable gravitational movement of DNAPLs.
- Minimize IDW.
- Mitigate similar types of collateral environmental damage inherent in addressing this complex environmental need.

Rapid Hydrophobic Sampling. Small diameter FLUTE™ membranes with hydrophobic sorbent (preferentially absorbs non-polar liquids) ribbons fixed to the liner are designed to collect DNAPL samples. The ribbon is impregnated with a DNAPL indicator dye for immediate assessment of the presence of DNAPLs at a specific depth. The system is fast and easy to deploy with a cone penetrometer system and yields depth-discrete samples from boreholes. The ribbon is pressed against the formation on the walls of the borehole, and the hydrophobic material preferentially collects organic liquids. The liner is then retrieved from the borehole and rapidly scanned visually and using a volatile organic compound (VOC) analyzer. After screening, the depth-discrete sorbent pads can be analyzed in more detail in the laboratory. The FLUTE™ can also be deployed using drilling methods.

Laser-Induced Fluorescence, Optical, and Raman Cone Penetrometer Methods. The cone penetrometer is particularly well suited for the characterization of DNAPL sites because of its relative ease in delineating depth-discrete lithology and contaminant distribution as well as its ability to deploy a variety of sensors. Although LIF sensors cannot directly measure chlorinated alkanes (because these

compounds do not fluoresce at standard excitation wavelengths), fluorescent intensities are found to increase (one to three orders of magnitude over background) in zones known to contain DNAPLs. This large increase may be due to the leaching of natural organic matter or the incorporation of other likely fluorophores into the DNAPLs. Co-disposed lubricants, hydraulic oils, and cutting oils are also potential candidates for fluorescence probing. Thus, the fluorescence measurements can be used to infer the presence of DNAPLs. Used in concert with Raman spectra, the presence of DNAPLs in a particular location can be confirmed.

Raman spectroscopy is one of the few direct-detection characterization technologies for DNAPLs. Each compound has a unique Raman spectrum that can be probed through the optics deployed in a cone penetrometer. Thus, specific DNAPL compounds can be identified. Unfortunately, the Raman technique is inherently weak, and the spectra must be separated from the often-dominating fluorescence spectrum.

Other optical techniques such as CPT video microscopy (Navy GeoVis™ system) have also helped identify DNAPLs in the subsurface. Specific formations can be visually identified for DNAPL potential for precise targeting by spectroscopy. If co-constituents color the DNAPLs, DNAPLs may be directly identified.

Small-Scale Alcohol Micro Injection/Extraction Test. The single-well, alcohol injection-extraction test in this program uses a cone penetrometer delivery system and less than one gallon of injection volume. The injected fluid, a solution of alcohol that can solubilize DNAPLs without mobilizing it, permeates into an area the size of a small cylinder around the cone penetrometer. A small volume of water is injected a small distance into the formation (less than 1 foot) and then extracted. Samples of the water are analyzed for concentrations of organic contaminants. Then, a small volume of an alcohol and water solution is injected a similar distance into the formation (less than 1 foot) and then extracted. The extracted solution is sampled and analyzed. DNAPLs will be much more soluble in the alcohol/water solution than in water alone. A large increase in the concentration of DNAPL components is an unequivocal indicator of the presence of residual DNAPLs. The test provides clear confirmation of DNAPLs without having to drill additional holes. The test has been used to target specific strata that were thought to contain DNAPLs (i.e., above clay in the saturated zone).

TECHNOLOGY NEED

Residual industrial solvents, primarily DNAPLs, are currently the most significant challenge for the successful completion of many large groundwater and soil cleanup efforts. Slowly dissolving DNAPLs provide a major source of groundwater contamination for hundreds of years. Adding to the challenge is the fact that DNAPLs are very difficult to characterize in the subsurface—especially when they are found in dispersed blobs as is typical at many sites. At waste sites where DNAPLs are suspected, robust characterization of the nature and extent of the contamination must be a key component of any comprehensive remediation strategy. Traditional sampling approaches generally are not successful at locating DNAPLs, and a focused strategy based on an appropriate conceptual model should be used. Above the water table, residual DNAPLs will reside in intergranular pores held by capillary forces. Below the water table, DNAPLs behave in a complex fashion, moving downward as an immiscible phase and accumulating in highly concentrated discrete and dispersed ganglia. Because of the physical and chemical characteristics of DNAPLs, characterization and remediation methods that minimize unnecessary waste generation are prudent. Finally, precise delineation of DNAPL areas will facilitate the design of appropriate remediation strategies and help keep cleanup costs from escalating. This work addresses STCG Need Statements:

OK99-01 - Characterization and Removal of Dense Non-Aqueous Phase Liquids (DNAPLs) and Light Non-Aqueous Phase Liquids (LNAPLs) from Soil and Groundwater

RL-SS25-S - Chemical Form and Mobility of Dense, Non-Aqueous Phase Liquids (DNAPLs) in Hanford Subsurface Transport of Contaminants

ORHY-01a - Dense Non-Aqueous Phase Liquids (DNAPLs) Source Characterization, Containment, and Treatment

ORHY-01b - Dense Non-Aqueous Phase Liquids (DNAPLs) Source Characterization, Containment, and Treatment

ORHY-01 - Dense Non-Aqueous Phase Liquids (DNAPLs) Source Characterization, Containment, and Treatment

SR99-3017 - Dense Non-Aqueous Phase Liquids (DNAPLs) Characterization and Remediation Technologies



This is a FLUTE™ membrane recovered from a cone penetrometer hole. The red marks indicate the presence of Dense Non-Aqueous Phase Liquids (DNAPLs) at that depth.

TECHNOLOGY BENEFITS

Many of the current baseline methods used for characterizing a suspected DNAPL site are described in Cohen and Mercer (1993). These methods generally consist of inferred measurements of DNAPLs (e.g., soil-gas analysis, geophysical methods), rule-of-thumb empirically developed methods from well samples, and direct measurements using invasive methods such as drilling and soil sampling. Most geophysical techniques do not have the resolution needed to detect DNAPLs occurring at scales of far less than one cubic meter. Conventional soil and liquid sampling is too costly and produces significant quantities of IDW.

Several of the techniques described here were designed specifically for implementation with the cone penetrometer. This takes advantage of the high-resolution geologic information that can be obtained with the cone penetrometer sensors and minimizes the production of IDW.

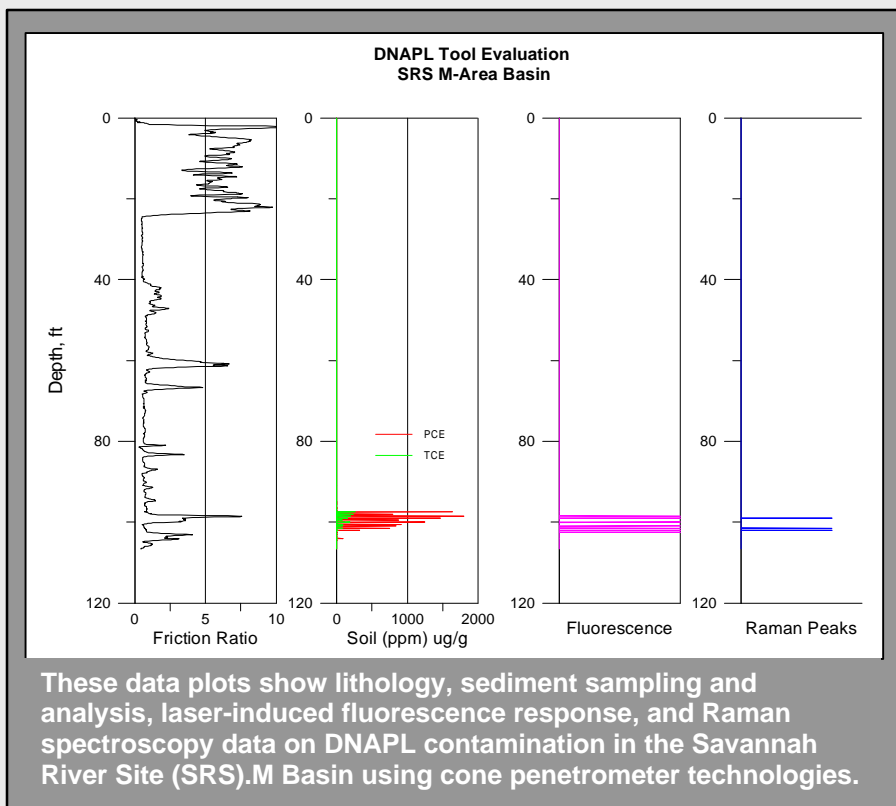
Because of the complexity of DNAPLs in the subsurface, all DNAPL characterization methods should be used in an ensemble approach where DNAPLs in an area are postulated with a probability determined from the weight of evidence of the data from several characterization techniques.

TECHNOLOGY CAPABILITIES/LIMITATIONS

By emphasizing safety and small-scale direct DNAPL detection, the technologies provide the most accurate possible information about the precise intervals where DNAPLS occurs, leading to optimized remediation design. The technologies in this task reduce waste and improve the precision of delineating DNAPL zones. The CPT optical technologies are limited to unconsolidated sediments and to depth refusal of the CPT truck. The CPT investigations are limited to the sediments in contact with the probe.

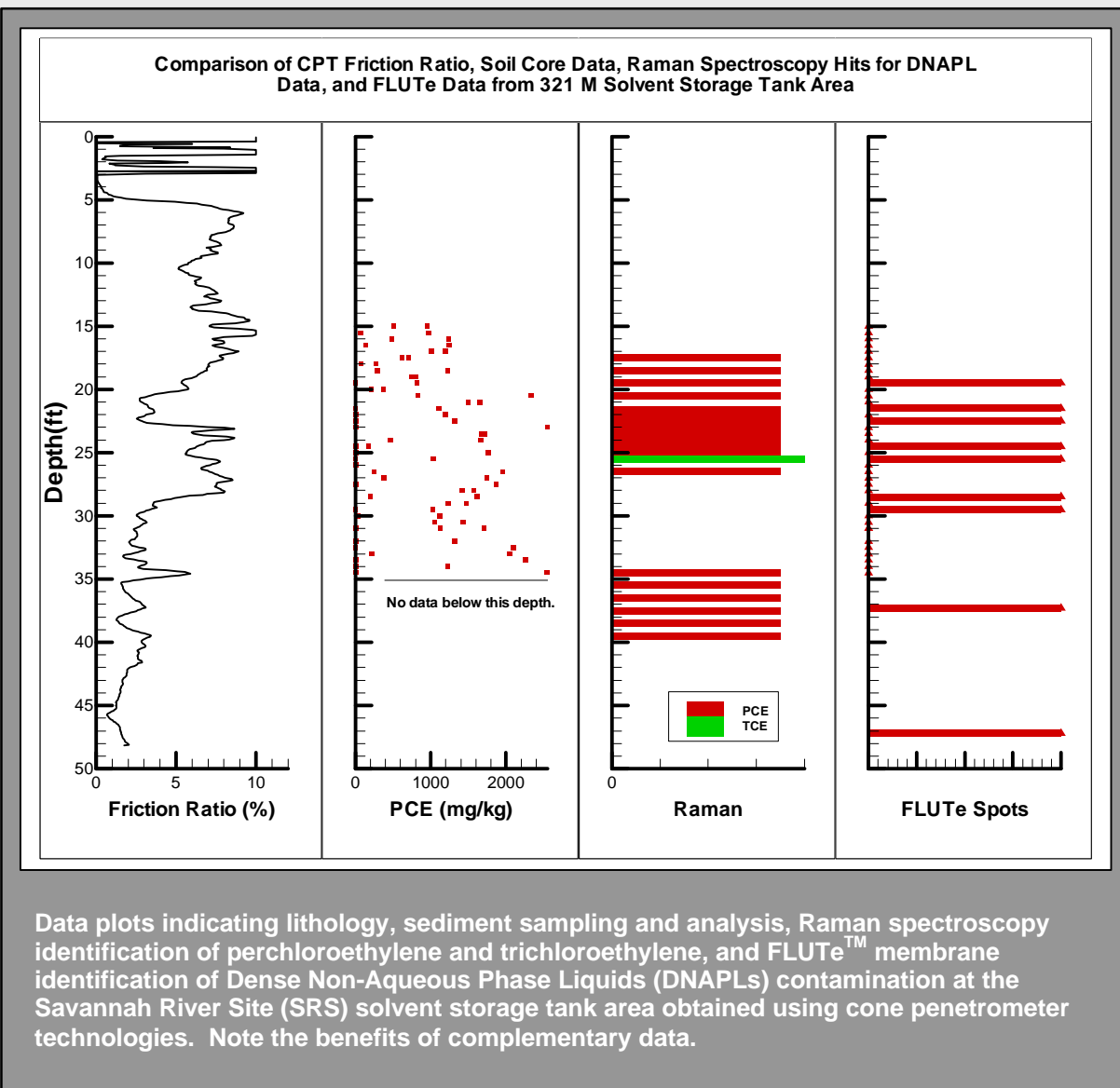
ACCOMPLISHMENTS AND ONGOING WORK

- First *in situ* direct detection of DNAPLs using FLUTE™ (membrane with dye-impregnated hydrophobic sorbent ribbon at SRS and Cape Canaveral.
- First *in situ* identification of perchloroethylene (PCE) and trichloroethylene (TCE) using Raman spectroscopy at the SRS and the Jacksonville dry cleaning site.
- Inferred detection of DNAPLs using LIF at multiple wavelengths at several waste sites.
- Developed library of fluorescence excitation and emission spectra of likely DNAPL co-constituents.
- First deployment of alcohol micro-injection/extraction test (PIX) through CPT for DNAPL detection at Cape Canaveral.
- Inferred detection of DNAPLs using differential partitioning gas tracer tests and quantitative limitations of this technique at SRS.
- First deployment of FLUTE™ (also known as SEAMIST™) membrane in a cone penetrometer hole.
- Development of DNAPL characterization course module for FY 1999.



COLLABORATION/TECHNOLOGY TRANSFER

This work is a collaborative effort between various federal agencies, universities, and private industry. Principal partners include Clemson University, EIC Laboratories Inc., FLUTE™ Limited, U.S. Army Corps of Engineers, Naval Facilities Engineering Service Center, Space and Naval Warfare Systems Center, U.S. Geological Survey, Applied Research Associates, Inc., Levine Fricke Inc., Tetra Tech Inc., Florida State University, Fugro Inc., Oak Ridge National Laboratory, and the EPA. Additional collaboration has been obtained from Duke Engineering Inc., the U.S. Air Force, and others. More than ten papers, presentations, and reports have been issued on work from this task to date and several more will be issued in the ensuing months.



TECHNICAL TASK PLAN (TTP) INFORMATION

TTP No./Title: SR17C221 - Development and Deployment of Innovative DNAPL Characterization Methods.

Related TTP No./Title.-.SR18SS32 - Applied DNAPL Characterization Methods; SR16C221 -SCAPS Logistics. The investigators on these tasks have collaborated successfully for many years and many useful technologies have emerged from these leveraged efforts.

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